Modification of epoxy-polyester and polyester powder coatings with silicone-acrylic nanopowders — effect on surface properties of coatings[*]

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Abstract: The effect of modification with 3 wt % of nanopowders containing silicone-acrylic core-shell nanoparticles (size ca. 100 nm) on surface properties of epoxy-polyester and polyester powder coatings was investigated. Contact angle (*CA*) determinations, atomic force microscopy (AFM), confocal microscopy (CM), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), and X-ray photoelectron spectroscopy (XPS) were used to assess this effect. It was found that the modified coatings showed significantly higher *CA* values and significantly lower surface-free energy (*SFE*) values as compared to unmodified ones what could be explained by migration of silicone resin contained in nanopowder to the coating surface due to specific features of silicone polymer. Using XPS and EDS the presence of silicone on the surface was confirmed, and AFM of modified coatings revealed structures on the surface which could be attributed to nanoparticles of silicone resin. It was stated that the chemical structure of silicone resin influenced very much surface properties of the coatings.

Keywords: coating, silicone, silicone-acrylic polymer, surface properties, nanopowders, core-shell particles.

Modyfikacja poliestrowo-epoksydowych i poliestrowych farb proszkowych za pomocą nanoproszków silikonowo-akrylowych — wpływ na właściwości powierzchni powłok

Streszczenie: Zaprezentowano wyniki badań wpływu modyfikacji poliestrowo-epoksydowych i poliestrowych farb proszkowych, za pomocą silikonowo-akrylowych cząstek o budowie rdzeń–otoczka, na właściwości powierzchni otrzymanych z nich powłok. Metodami mikroskopii konfokalnej (CM) i mikroskopii sił atomowych (AFM) określono topografię, a za pomocą skaningowego mikroskopu elektronowego wyposażonego w spektrometr dyspersji energii (SEM-EDS) oraz spektroskopu fotoelektronów (XPS) badano skład pierwiastkowy. Metodą kropli osadzanej wyznaczono kąt zwilżania (*CA*) i swobodną energię powierzchniową (*SFE*). Stwierdzono, że modyfikacja farb proszkowych za pomocą silikonowo-akrylowych nanocząstek polimerowych wpływa na zwiększenie wartości *CA* oraz zmniejszenie wartości *SFE*, co może być spowodowane migracją żywicy silikonowej do powierzchni powłoki. Obecność silikonu na powierzchni próbki potwierdzono za pomocą EDS, a badanie XPS wykazało tendencję do zwiększania się ilości silikonu w powłoce w kierunku powierzchni próbki. Zauważalny jest również wpływ modyfikatorów silikonowo-akrylowych na strukturę powierzchni.

Słowa kluczowe: powłoka, silikon, polimer silikonowo-akrylowy, właściwości powierzchni, nanoproszki, cząstki rdzeń–otoczka.

Powder coatings are environmentally friendly replacements for solvent-based coatings and are commonly used to protect metal, plastic and other surfaces from mechanical and weather-related damage in certain industry sectors including, inter alia, the automotive or machine industry. Main components of powder coatings are polymer resins, curing agents, colorants and other additives [1] and the coating composition can be designed to obtain the desired coating properties. Nanoadditives have recently been recommended for use in the coating process to improve coating durability as well as its appearance [2—5]. Powder coatings modification with core-shell structured silicone-methacrylic nanoparticles (NP) developed in the Industrial Chemistry Research Institute led to coatings characterized by distinctly higher elasticity

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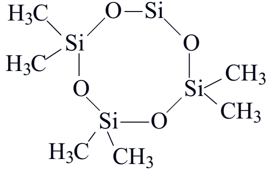
[**)] Author for correspondence; e-mail: izabela.ofat@ichp.pl and impact resistance than unmodified products [6, 7]. The idea to apply NP as an effective powder coatings modifier, patented first by Wacker [8], was based on the assumption that using the core-shell nanoparticles, where silicone resin of low glass transition temperature (T_g) constitutes the core and methacrylic polymer of high T_g constitutes the shell, would allow to achieve good distribution of the former in the coating matrix thus leading to excellent ability of the coating to absorb high mechanical stresses created by impact forces. The well known specific characteristics of polysiloxanes [9] predispose siloxane polymers not only to act as suitable impact modifiers in polymer-based composite materials, but also to change their surface properties significantly [10—14]. In this paper the results of our studies on the effect of chemical composition of silicone resin (i.e. the polysiloxane core of our NP modifier) on surface properties of epoxy-polyester and polyester powder coatings are presented. Some results obtained in these studies were presented at ICANM2013 Conference in Quebec City (Canada) and published [15].

EXPERIMENTAL

Materials

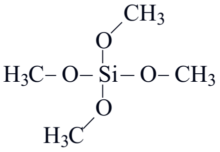
Octamethylcyclotetrasiloxane [D4 — formula (I), from Momentive], methyltrimethoxysilane and methacryloyltrimethoxysilane [METMS — formula (II) and MATMS — formula (III), respectively, both from Acros Organics], dodecylbenzenesulphonic acid (DBSA, from Aldrich), sodium hydrogen carbonate (from POCh) and Acticide® MBS (from Thor) were used as starting materials for synthesis of silicone resin dispersion.

Methyl methacrylate (MM, from HEKO), potassium persulphate (POCh), DBSA and Acticide® MBS were used as a monomer, initiator, surfactant and biocide for synthesis of silicone-acrylic core-shell dispersion.



(I)

difunctional



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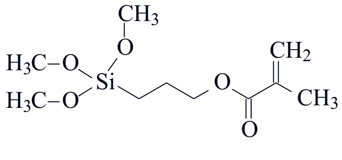

(III)

trifunctional

Powder coatings were obtained from carboxylated polyester resin (Policen 3000T, characterized by acid value 33 mg KOH/g, from PPG Polifarb Cieszyn), epoxy resin (Epidian® 012, from Organika-Sarzyna), Primid® XL 552 (from EMS-Chemie AG, used as hydroxyalkylamide crosslinker for polyester coatings), TiO_2 (Rutile, from Police, Poland, used as a pigment). Benzoin (from DSM) and Resiflow® PV 88 (from Worlee Chemie GmbH) were used as standard additives for powder coating.

Synthesis of starting silicone-resin dispersions, hybrid dispersions and silicone-methacrylic nanoparticles

Aqueous dispersions of silicone resin nanoparticles of ca. 80 nm size were synthesized through emulsion polymerization of silicone monomers in water, according to the method proposed by Weyenberg et al. [16]. DBSA was used as both catalyst and surfactant. Compositions of silicone monomers mixtures are collected in Table 1. Vacuum distillation was applied to remove methanol that was formed in hydrolysis of alkoxysilane group. Acticide® MBS was added as microbiological preservative.

Table 1. Composition of silicone monomers mixtures used in preparation of NP samples

Monomer	NP-1	NP-2
MATMS, wt %	0.0	14.6
METMS, wt %	12.0	5.4
D4, wt %	88.0	80.0

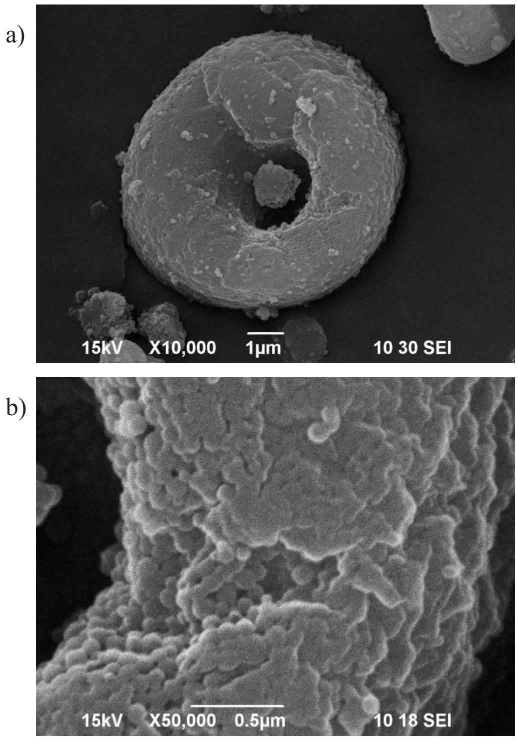

Fig. 1. NP nanoparticles agglomerated in the „nanopowder" particle: a) magnification 10 000×, b) magnification 50 000×

In the next step emulsion polymerization of methyl methacrylate in silicone resin dispersion was carried out as presented in [17], leading to aqueous dispersion of core-shell structured NP. Then, core-shell aqueous dispersion thus obtained was dried using Buchi spray dryer. In this process nanopowder agglomerates of the spherical NP of grain size from 1 to 20 μm were obtained (see Fig. 1).

Preparation of powder coatings

Epoxy-polyester and polyester powder coatings were produced in a standard process which involved:

— pre-mixing of components (compositions are presented in Table 2),
— extrusion (extruding temperature 80—100 °C),
— crushing,
— pulverizing,
— sieving,
— electrostatic spraying on metallic substrates.

Earlier we found [6] that increasing the content of nanopowder in powder coatings from 1 to 5 % resulted in significant changes in surface properties of the cured coating. We also proved that modification with just 3 % of nanopowder led to distinct improvement of substantial coating properties (impact resistance, elasticity) while not deteriorating the other coating features (hardness, abrasion resistance). Therefore, we decided to study the effect of silicone resin composition on surface properties of the powder coatings containing only that specific optimum amount of NP.

Table 2. Composition of prepared powder coatings

Ingredient	Polyester powder coating	Epoxy-polyester powder coating
Epoxy resin, wt %	—	22.21
Carboxylic polyester hardener, wt %	—	51.83
Polyester resin, wt %	56.05	—
Hardener, wt %	2.95	—
TiO_2, wt %	37.00	22.21
Standard additives, wt %	1.00	0.74
NP[a)], wt %	3.0	3.0

[a)] Applicable only to modified samples.

Coatings were cured for 15 minutes at 180 °C.

In Table 3 the obtained powder coating samples with their designations are shown.

Table 3. Designation of unmodified and modified powder coating samples

NP modifier	Polyester powder coating	Epoxy-polyester powder coating
None	P-0	H-0
NP-1	P-1	H-1
NP-2	P-2	H-2

Characterization of cured coatings

Thickness of cured coatings was measured with PosiTector 200 ultrasonic thickness gauge according to ISO 2808 standard. For comparative studies coatings with similar thickness (60—90 μm) were chosen.

Surface elemental composition was determined by scanning electron microscopy equipped with energy dispersive spectrometry (SEM-EDS) using Jeol JSM-6490LV microscope and by X-ray photoelectron spectroscopy (XPS) using ESCALAB-210 apparatus.

Coatings surface appearance was tested by atomic force microscopy (AFM) using the Multimode NS3D microscope and by confocal microscopy using confocal microscope NanoFokus AG μSurf Explorer.

Morphologies of the surfaces were determined using confocal microscope with applied 50x magnification, and topographic maps in 0.59 mm × 0.59 mm area were taken. The roughness parameters (R_a — arithmetic mean roughness value, R_z — maximum height of profile, P_{sm} — arithmetic mean width of the roughness profile elements, P_{dq} — root-mean-square surface gradient of the profile within a sampling length, P_t — the distance between the highest peak and the deepest valley of the profile) were determined according to ISO 4287 standard.

Contact angle (*CA*) of water and diiodomethane on cured coatings was examined using Kruss DSA100E goniometer. Surface free energy (*SFE*) values, including its polar and dispersive parts, were calculated based on the *CA* data.

RESULTS AND DISCUSSION

Results of SEM-EDS and XPS studies conducted for the epoxy-polyester PC are presented in Fig. 2 and in Fig. 3, respectively.

Based on the SEM-EDS results shown in Fig. 2, which have been obtained in testing the unmodified powder coating (H-0) and two different NP-modified powder coating samples (H-1 and H-2), it has been confirmed that modification with 3 % of NP resulted in the apparent change of elemental composition of coating surfaces no matter what the composition of silicone resin was. The results of EDS investigations presented in Fig. 2a proved that concentration of O and Si atoms was much higher and concentration of C atoms was lower on the surface of powder coatings modified with NP than on the surface of unmodified sample. EDS maps of Si element showed that Si atoms were not uniformly distributed on modified samples surfaces which could result from poor miscibility of silicones within the polymer matrix. This observation is also reflected in EDS spectra (Fig. 2c). The presence of Ti atoms on the powder coating surface, which was noted in [15], was also observed for the samples tested and can be considered as obvious since TiO_2 was a component of the coating recipe. Those results clearly proved that surface features for powder coatings modified with

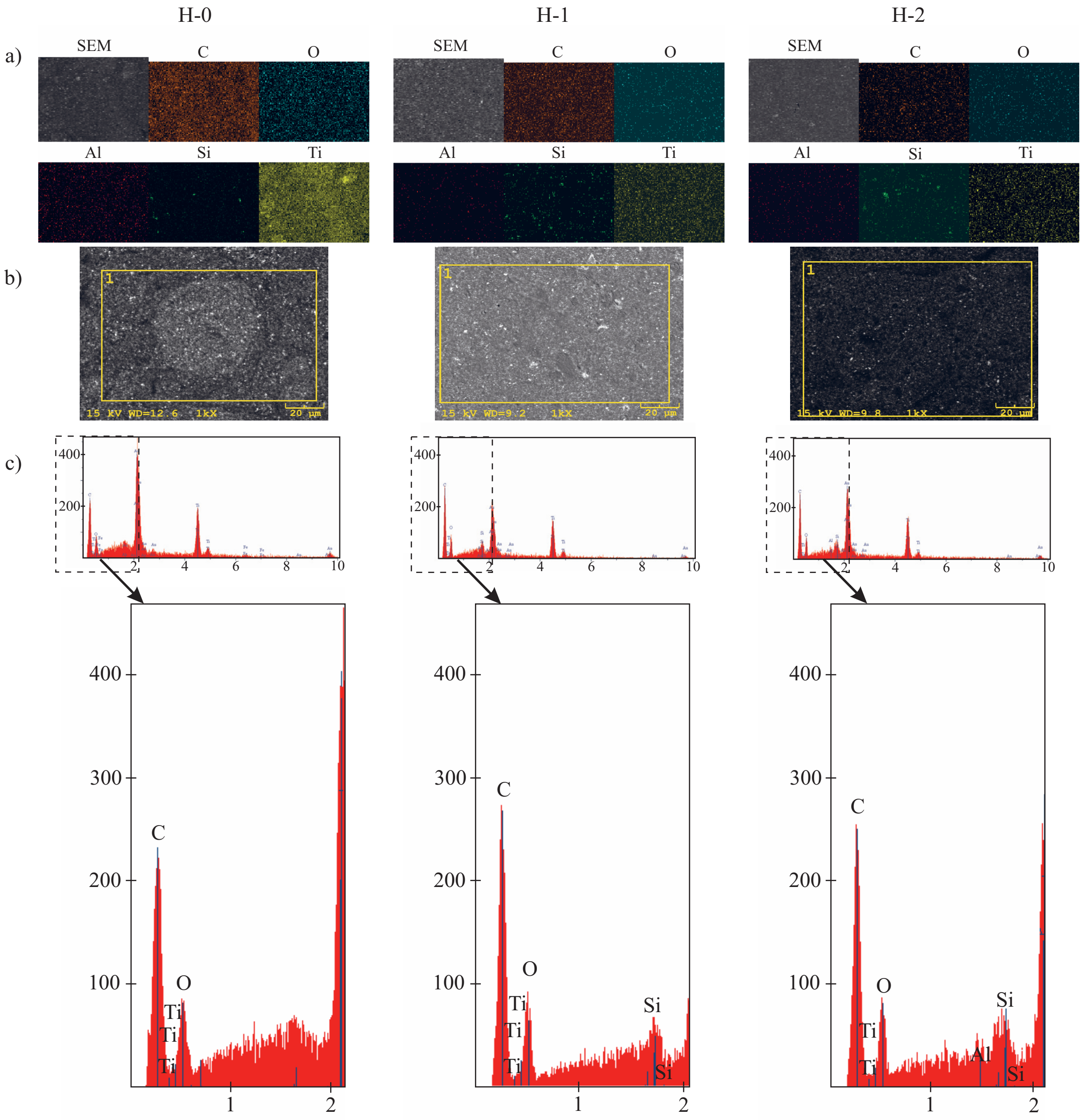

Fig. 2. Elemental composition of surfaces of modified and unmodified epoxy-polyester powder coating assessed by SEM-EDS for H-0, H-1 and H-2 samples: a) elements distribution images — magnification 500×; b) SEM images — magnification 1000×; c) EDS spectra — magnification applied 1000× with relevant details of EDS spectra

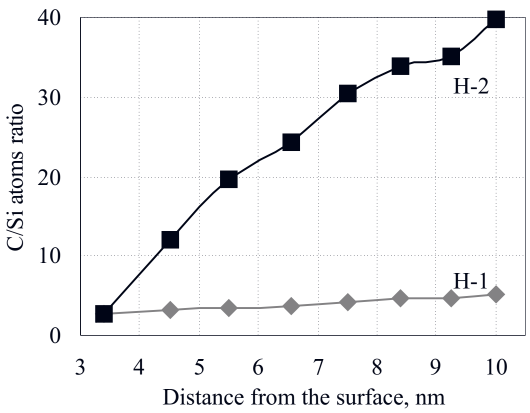

Fig. 3. Influence of the distance from the surface on the determined by XPS carbon to silicon atoms content ratio (C/Si) for H-1 and H-2 samples

NP were the same, despite the composition of silicone resin contained in the sample tested.

According to XPS results, shown in Fig. 3, silicone resin migration to surfaces of samples modified with NP containing silicone resin with different composition could be observed. The content of Si atoms (correlated with C atoms content) at a very close distance to the surface was much higher than few nanometers deeper in the bulk of coating while even that value, specifically for H-1 sample, was very much higher than the value representing the average Si atoms content in the modified coating recipe, what is evident from results listed in Table 4. For unmodified sample Si atoms were not detected by XPS.

Quite significant difference between Si concentration on the surface observed for H-1 and H-2 samples can be

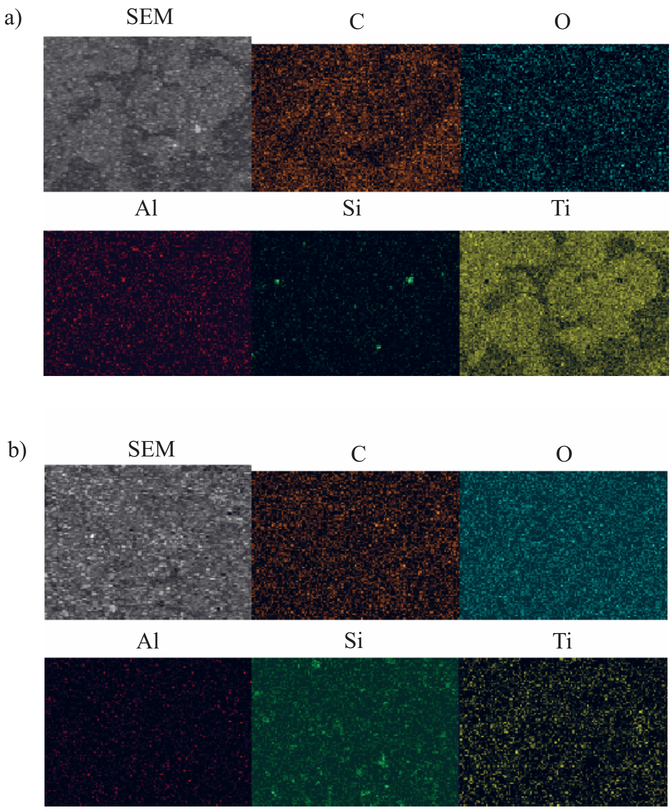

Fig. 4. Assessed by SEM-EDS elements distribution images (magnification 500×) on surfaces of samples: a) P-0, b) P-2

explained by difference in silicone resin structure in both cases. In case of H-1 the silicone resin had more hydrophobic and less polar character due to absence of less hydrophobic and more polar silicone monomer (MATMS) in starting composition of silicone monomers what resulted in lower compatibility of silicone resin with the polymer matrix of powder coating and eventually led to easier migration of the resin to the coating surface.

Results of SEM-EDS and XPS studies conducted for polyester coatings are presented in Fig. 4 and 5, respectively.

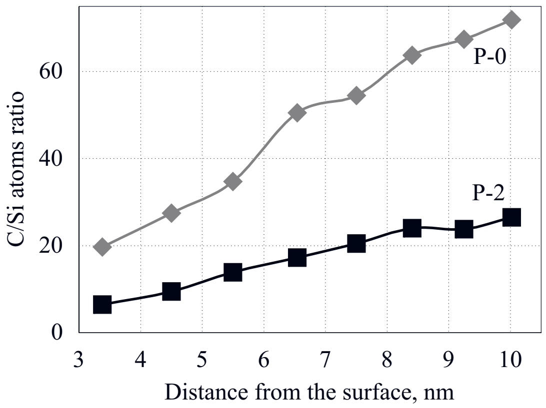

Fig. 5. Influence of the distance from the surface on the determined by XPS carbon to silicon atoms content ratio (C/Si) for P-0 and P-2 samples

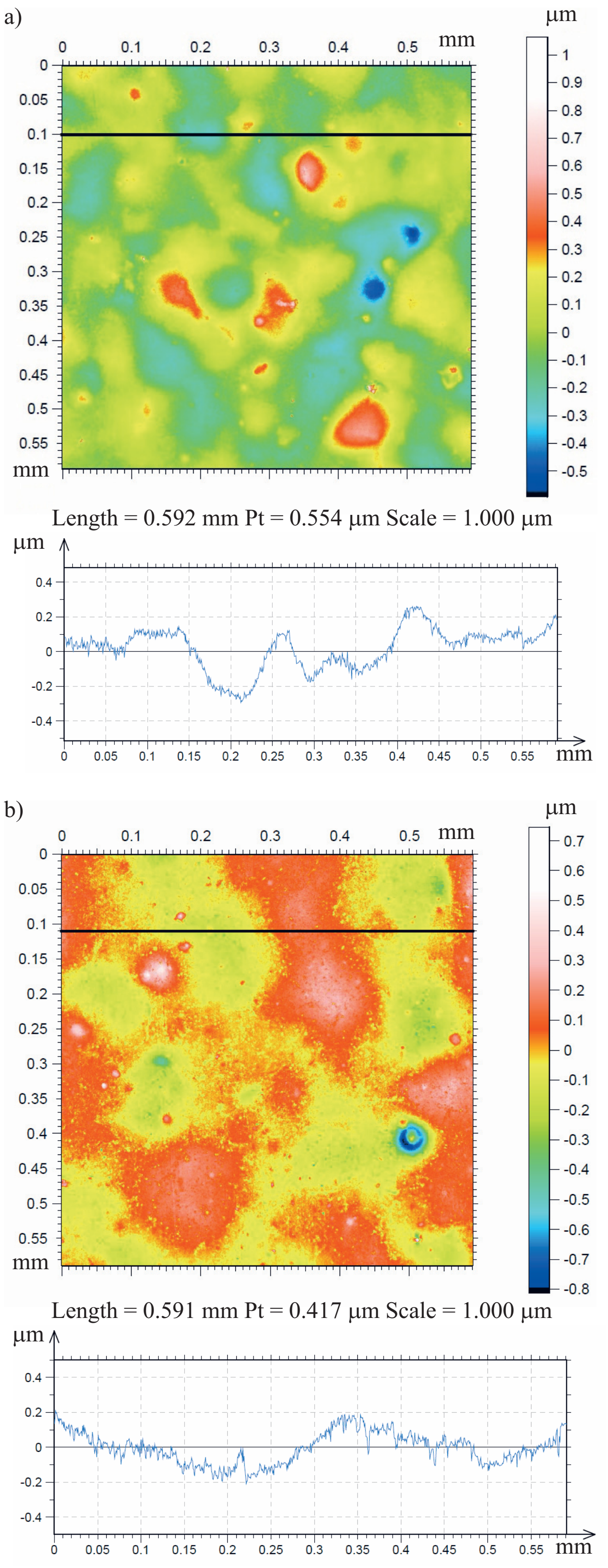

Fig. 6. Determined by confocal microscope powder coating surface topography layers with profiles for samples: a) H-0, b) H-1

Similarly as in the case of epoxy-polyester coatings the concentration of Si and O atoms on surfaces of polyester coatings modified with NP (P-2 sample) is much higher than for unmodified (P-0 sample). XPS studies (Fig. 6)

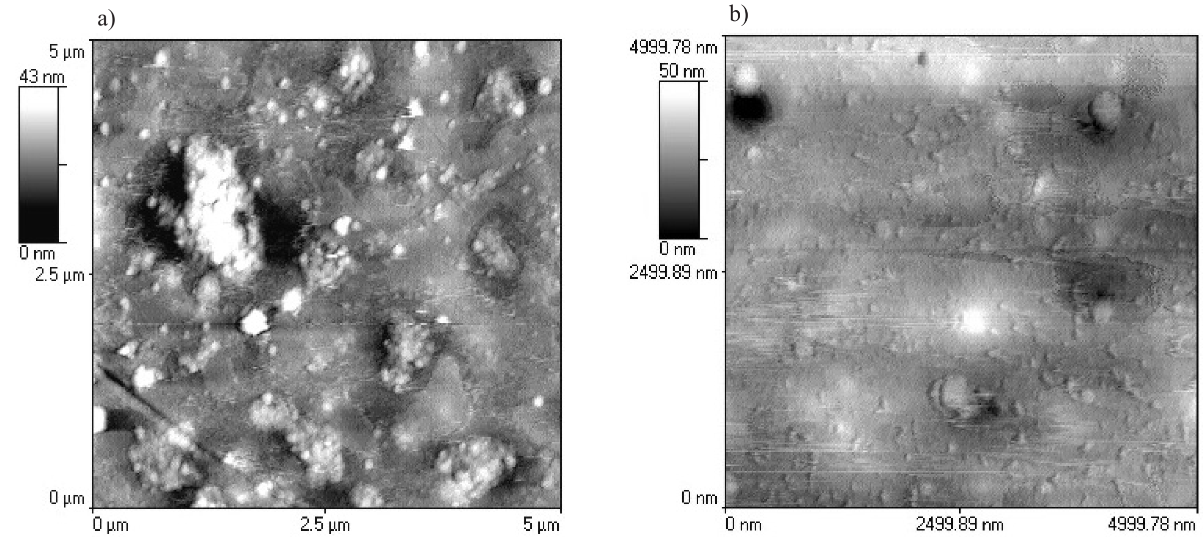

Fig. 7. AFM images for samples: a) H-0, b) H-1

confirmed that Si atoms content (correlated with the amount of C atoms) decreased with increasing distance from the surface.

Morphology of the surface of prepared power coating samples was investigated using confocal microscope. In Fig. 6 the contour plot maps of epoxy-polyester powder coatings surfaces are shown. For better determination of surfaces appearance micrometer scale topographic profiles were generated along the lines marked on the topography maps.

Table 4. Concentration of Si atoms at the different distance from the surface for H-1 and H-2 samples

Distance from surface, nm	Si atoms content, %	
	H-1	H-2
3.4	22.30	24.58
4.5	19.70	6.37
5.5	18.00	4.06
6.5	16.30	3.30
7.5	15.00	2.63
8.4	13.80	2.34
9.2	13.40	2.24
10.0	12.70	1.98
11.3	12.50	1.99

Table 5. Roughness parameters for H-0 and H-1 samples

Roughness parameters	H-0	H-1
R_a, nm	82	43
R_z, nm	377	269
P_t, nm	554	417
P_{sm}, µm	48	21
P_{dq}, °	1.75	2.27

From the results shown in Fig. 6 and roughness parameters listed in Table 5, it seems clear that modification with NP significantly affected the structure of powder coatings surface, making the surface smoother. In the level plot graphs we can see higher variation in the elevation of the unmodified coating sample across the tested region, and an area of the deep valley (level lower than -0.1 µm) and of the hills (level higher than 0.1 µm) is higher too. The surface structure of modified sample is more regular, hills and valleys with tighter diameter then in the case of unmodified sample (what was confirmed by P_{sm} value), and level difference is lower (distance from the lowest to the highest point is 417 nm) than for unmodified coatings where that distance is 554 nm. The nanostructure of the coating surface was studied by AFM. The nanostructure of H-0 and H-1 samples, presented in Fig. 7, looks quite different. On the surface of the unmodified sample (H-0) there are several islands which average size is about 500—1000 nm while on the modified surface lots of bulges can be observed with average diameter of about 80—200 nm. Moreover, it seems clear that the modification led to improved composite homogeneity.

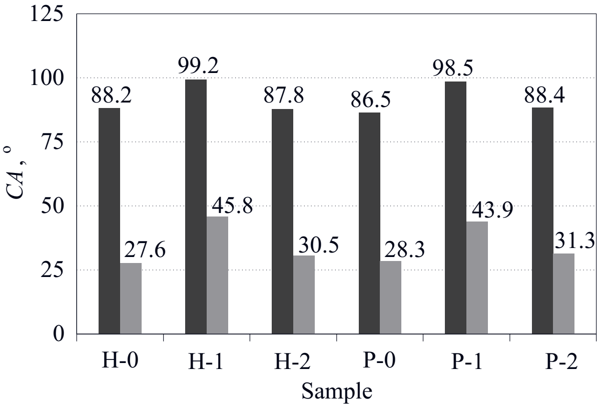

Fig. 8. Contact angle (*CA*) of water (black) and diiodomethane (grey) sessile droplet on prepared powder coating samples

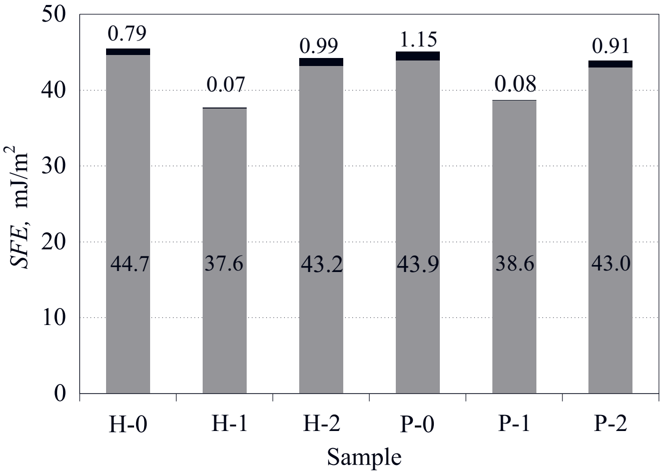

Fig. 9. Polar (γ_p — black) and dispersive (γ_d — grey) parts of surface free energy (*SFE*) of prepared powder coating samples

Finally, *CA* of the modified and unmodified powder coatings was determined at the ambient temperature using sessile drop method for water and diiodomethane. *SFE* with its parts (polar γ_p and dispersive γ_d) was calculated using Owens-Wendt method. Results are shown in Fig. 8 and 9.

As it can be concluded from the results presented in Fig. 8 and 9, the modification of powder coatings with highly hydrophobic and low-polar silicone resin which migrated easily to the coating surface resulted in very significantly increased *CA* value and decreased *SFE* value observed for H-1 sample. For coatings modified with more polar and less hydrophobic silicone resin (samples H-2 and P-2) those differences were much less distinct.

CONCLUSIONS

Modification of epoxy-polyester and polyester powder coatings with silicone-poly(methyl methacrylate) core-shell NP was performed. It was found through SEM-EDS and XPS studies that such modification led to a change in chemical composition of coating surfaces what indicated that silicone resin migrated to the surface. That effect was much more significant for the coatings modified with NP containing more hydrophobic and less polar silicone resin. Similar observations were made with regard to the results of studies on the effect of modification of the coatings with NP on surface profiles and contact angles.

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